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Agersted, Karsten

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# Sintering doped Ceria in air

K. Agersted

Institute for Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark

## Abstract

Thermo kinetic software was used to evaluate the sintering mechanisms when Gadolinium-doped and Samaria-doped ceria powders (Rhodia, HSA and Fuel Cell Materials, SDC-TC, respectively) were sintered with two additives, Manganese oxide and Copper oxide, to control densification behaviour, i.e. promoting densification and grain growth during earlier stages of sintering as compared to sintering powders with no additives. Results indicate that grain boundary mobility was activated by the added promoters and that sintering mechanisms depend on the grain boundary chemistry, ie. the sintering aid.

## Introduction

Analysis of the sintering kinetics through the thermokinetic software “Kinetic3” may have both technical purposes, eg. for data reduction and to predict sintering behaviour, and be used for more in-depth analysis of the individual mechanisms of the overall process. The conversion function,  $U(t, T, a(r), a(p))$  is modeled through approximating and separating the conversion in to separate functions:

$$U(t, T, a(r), a(p)) = f(T(t)) \cdot g(x),$$

which are dependent on temperature profile,  $f(T(t))$ , and degree of conversion, respectively. The conversion dependency may be modeled through a range of well established reaction mechanisms, of which the simplest is a first-order reaction, and the temperature dependent term is described by the well known Arrhenius equation,  $f(T) = A \cdot \exp(-E/RT)$ . Additionally, a model-free approximation of the activation energy may be derived, e.g. using the FRIEDMAN analysis [Friedman (1965)] including evaluation of the pre-exponential factor,  $A$ , assuming a first-order reaction.

The use of transition metal oxides for controlling the sintering behaviour of ceria has been reported [Kleinlogel & Gauckler (2000), Hardy, J.S. et al (2011)] and is often used to promote sintering at lower temperatures (Li, Cu, Co) or to control the region of maximum sintering activity at specific higher temperatures (Fe, Mn), which in this case is of interest for a successful co-sintering of dual-layer electrolyte structures from zirconia- and ceria-based materials, which may alleviate the high oxygen activity that has been shown to build up during high temperature electrolysis in zirconia-based electrolytes against the oxygen electrode [Mogensen & Jacobsen (2009), Virkar (2010), Knibbe et al (2010)] and which seems detrimental to achieving life times at commercially interesting levels.

Hence, the work aims at characterizing the sintering behaviour qualitatively and later through modelling of gadolinium doped ceria powders (CGO10, Rhodia HSA) and and Samaria doped ceria (SDC20, FuelCellMaterials SDC-TC & SDC-HP) with sintering controlled through addition of Cu and Mn. Oxides.

## Experimental

Powders CGO10, ( $S_w = 23 \text{ m}^2/\text{g}$ ,  $d_{50} = 0.45 \mu\text{m}$ ), SDC-TC ( $S_w = 7 \text{ m}^2/\text{g}$ ,  $d_{50} = 0.4 \mu\text{m}$ ) or SDC-HP ( $S_w = 12 \text{ m}^2/\text{g}$ ,  $d_{50} = 0.38 \mu\text{m}$ ) were mixed in ethanol with sintering aids ( $\text{MnCO}_3$  or  $\text{CuO}$ ) in a ball mill for ~18 hours, dried and pressed both uniaxially and isotatically into samples with TD~0.6 and lengths of approximately 7.5 mm, which fitted into the double pushrod dilatometer, NETZSCH model 402 CD. Sintering in duplex was performed in flowing air at heating rates relevant for later processing (1, 5, 10 °C/min) and in cases also at 0.33 °C/min and 20 °C/min. Powders without sintering aids were heated from room temperature to ~1500°C and powders with sintering aids to 1300 °C or 1400 °C.

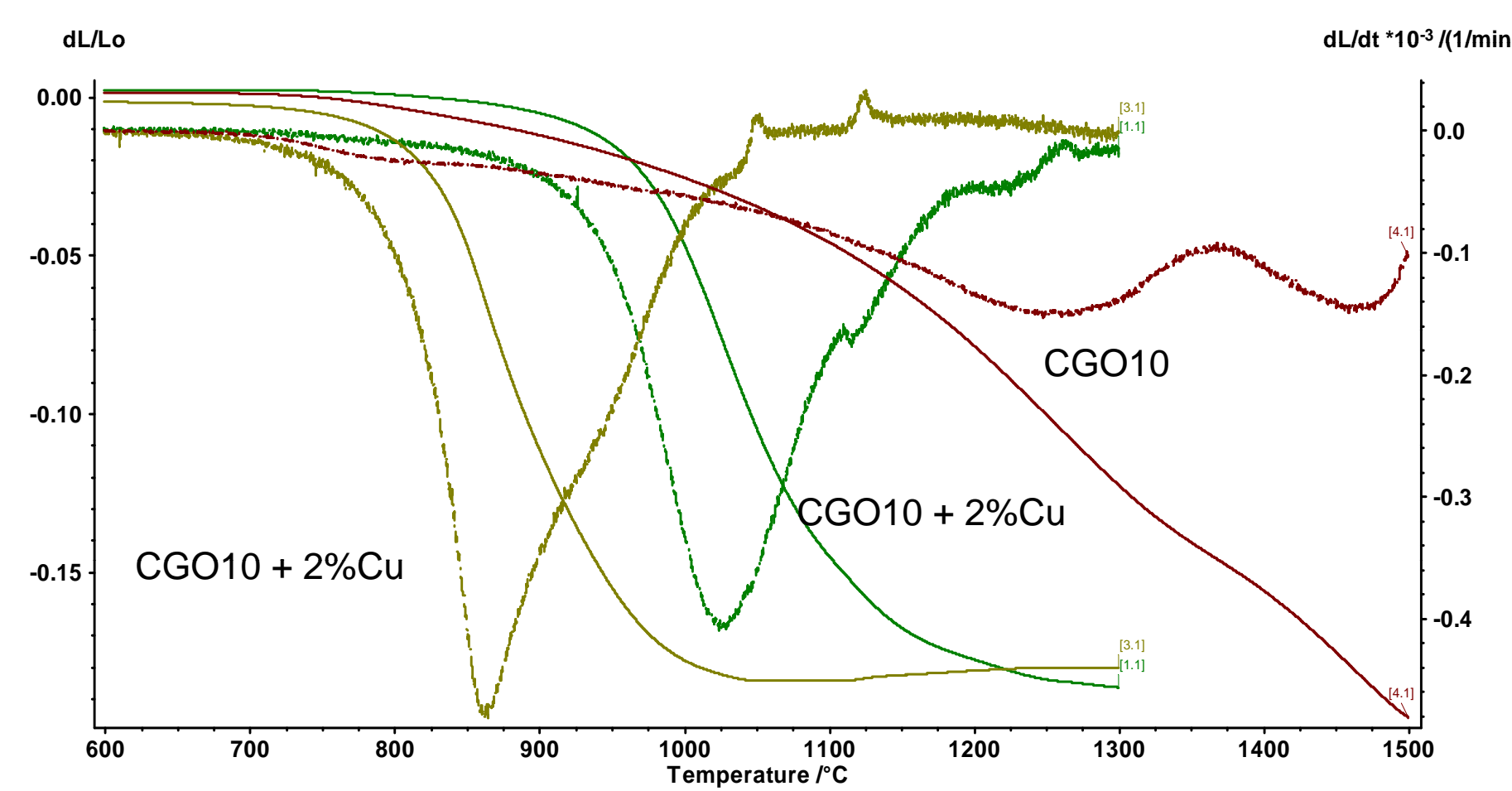
## Results and Discussion

Figure 1 illustrates the marked impact from sintering aids on both the sintering rates and on the temperature of maximum sintering rate. In Figures 3-4 are shown the results from a model-free calculation of the kinetic field, Friedman (1935), for which the primary results, the activation energy plot, has been exemplified in Figure 2.

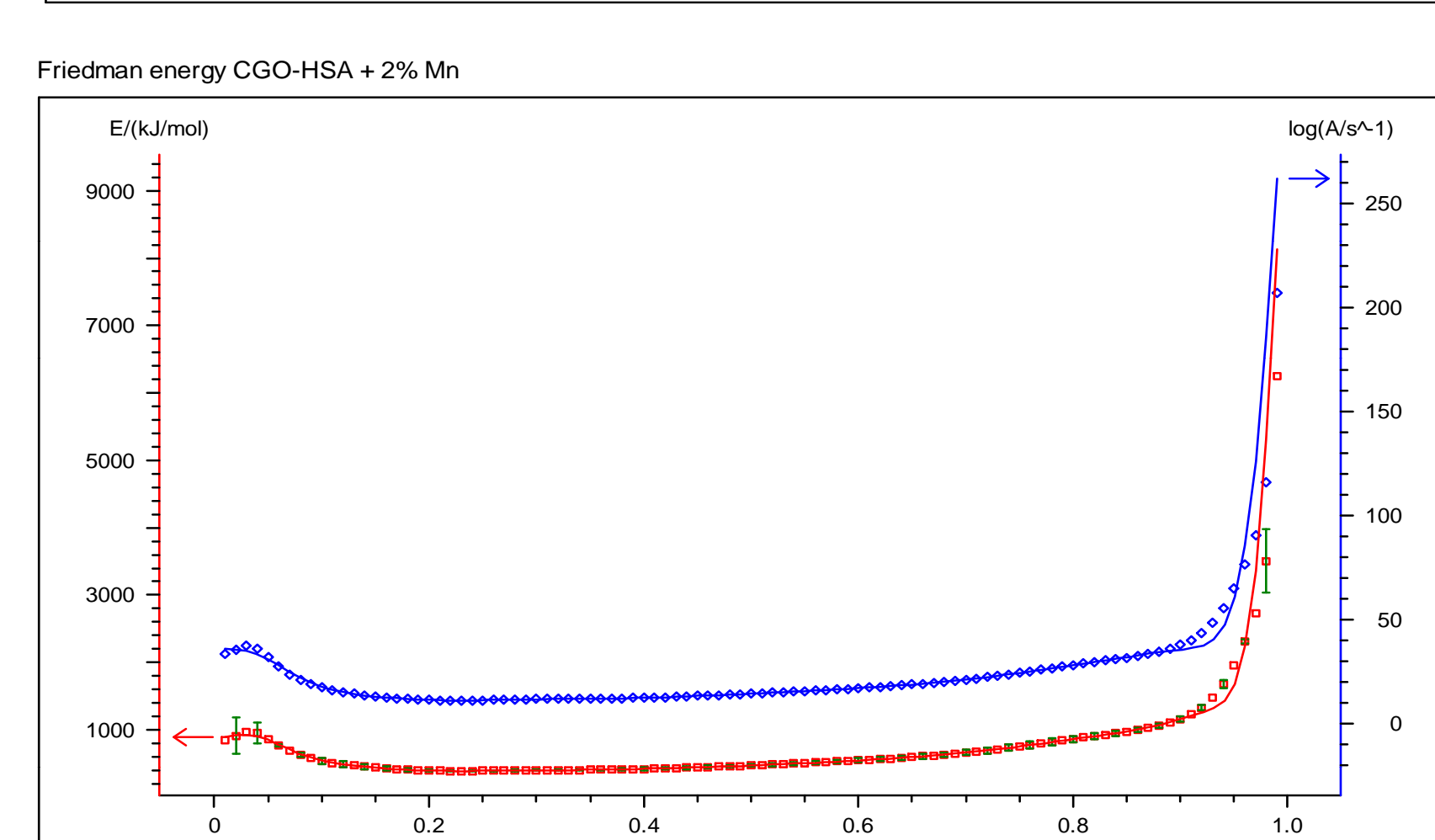
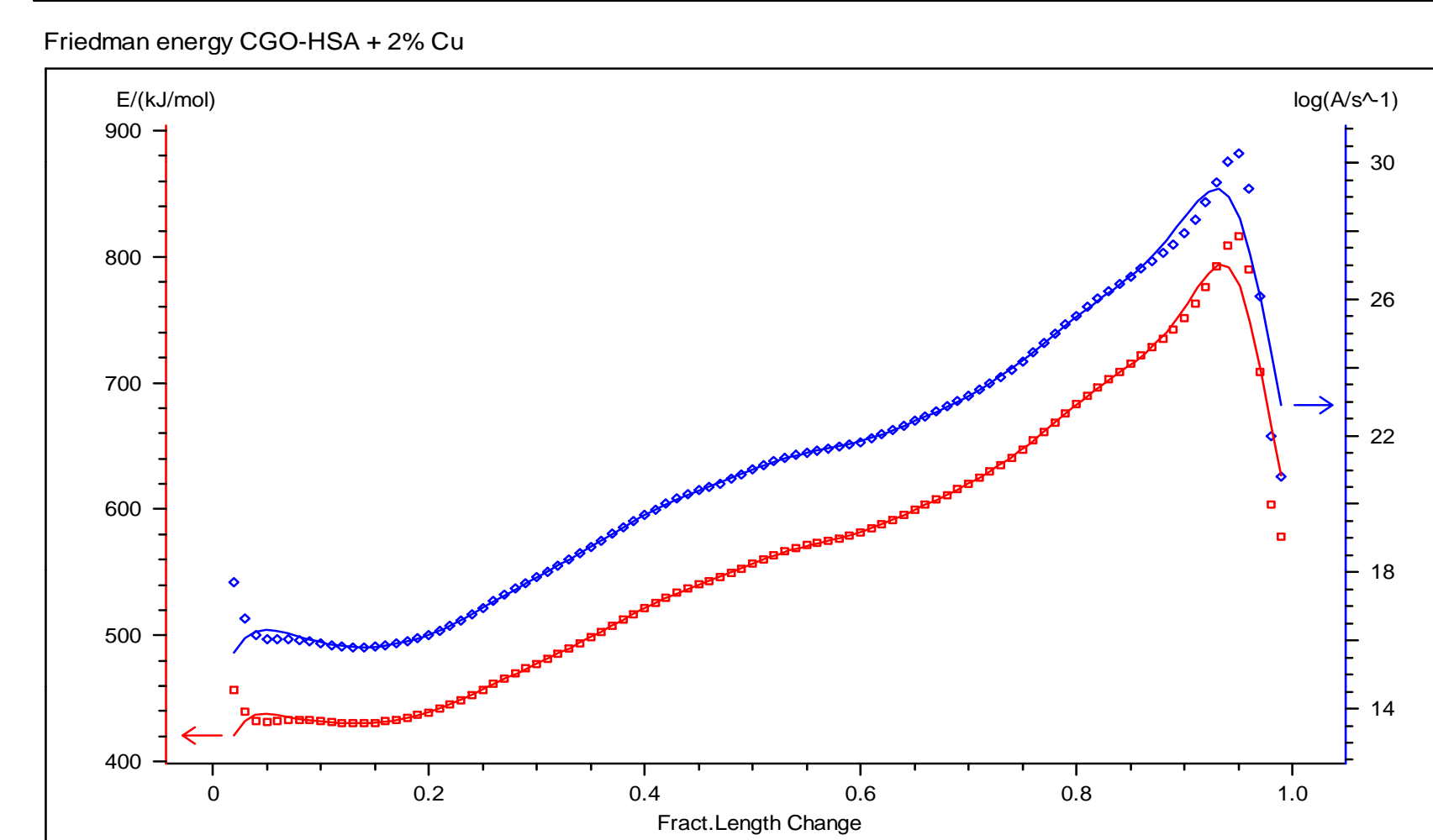
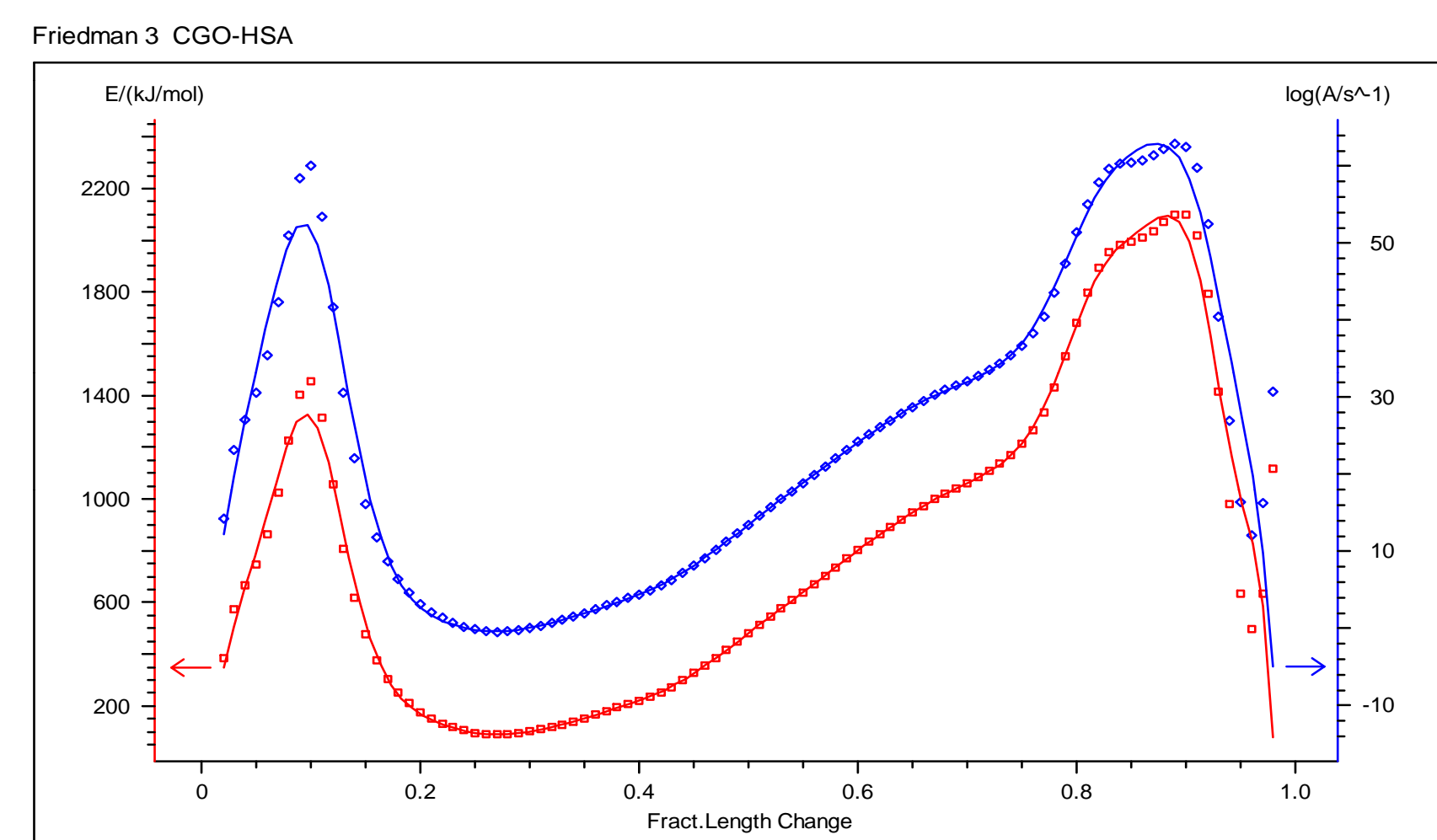
Sintering CGO10 at 1-10 °C/min CGO to final densities between 89%TD and 96%TD shows only very low activation energies, much like shown in Figure 4 for SDC-HP, but if lower heating rate(s) are included (0.33 °C/min) a marked change is seen, which is shown in upper most part of Figure 3 indicating that lattice diffusion with high activation energy becomes an important densification mechanism towards the end of densification. A similar trend, but at a lower level of activation energies, is observed for the sintering of CGO10 with Cu-addition. In contrast, activation energy stays at a constant high level almost throughout the densification of CGO10 with Mn-addition, which also reaches the highest level of density, ~96%TD. In general, both SDC-HP and CGO10 powders reaches final

densities, which depend on sintering aid but only little on the applied heating rates in the interval 1-10 °C/min. In contrast, sintering the SDC-TC powder is sensitive heating rates, cf. figure 4 bottom, and seems controlled by at least two parallel mechanisms. Further, the trend of the activation energy for SDC-HP powder shows relative low levels towards the end of densification, which is in contrast to CGO10, and may be attributed to the somewhat lower densities (~87%TD) reached for this powder. Various levels of Mn-additions (0%, 0.5%, 1%, 2%) were tried on SDC-powders (not shown here) and resulted in significantly higher density to be reached for addition of 0.5%Mn than any of the others, why only these results are shown here. Other investigations (Mr. Ni, this conference) showed activation energies,  $E_a = 450\text{--}480 \text{ kJ/mol}$ , throughout sintering CGO10 powders could be attributed to the grain growth, but more than one mechanism is obviously responsible for the overall densification process, as indicated by the non-constant levels of activation energies generally observed for samples.

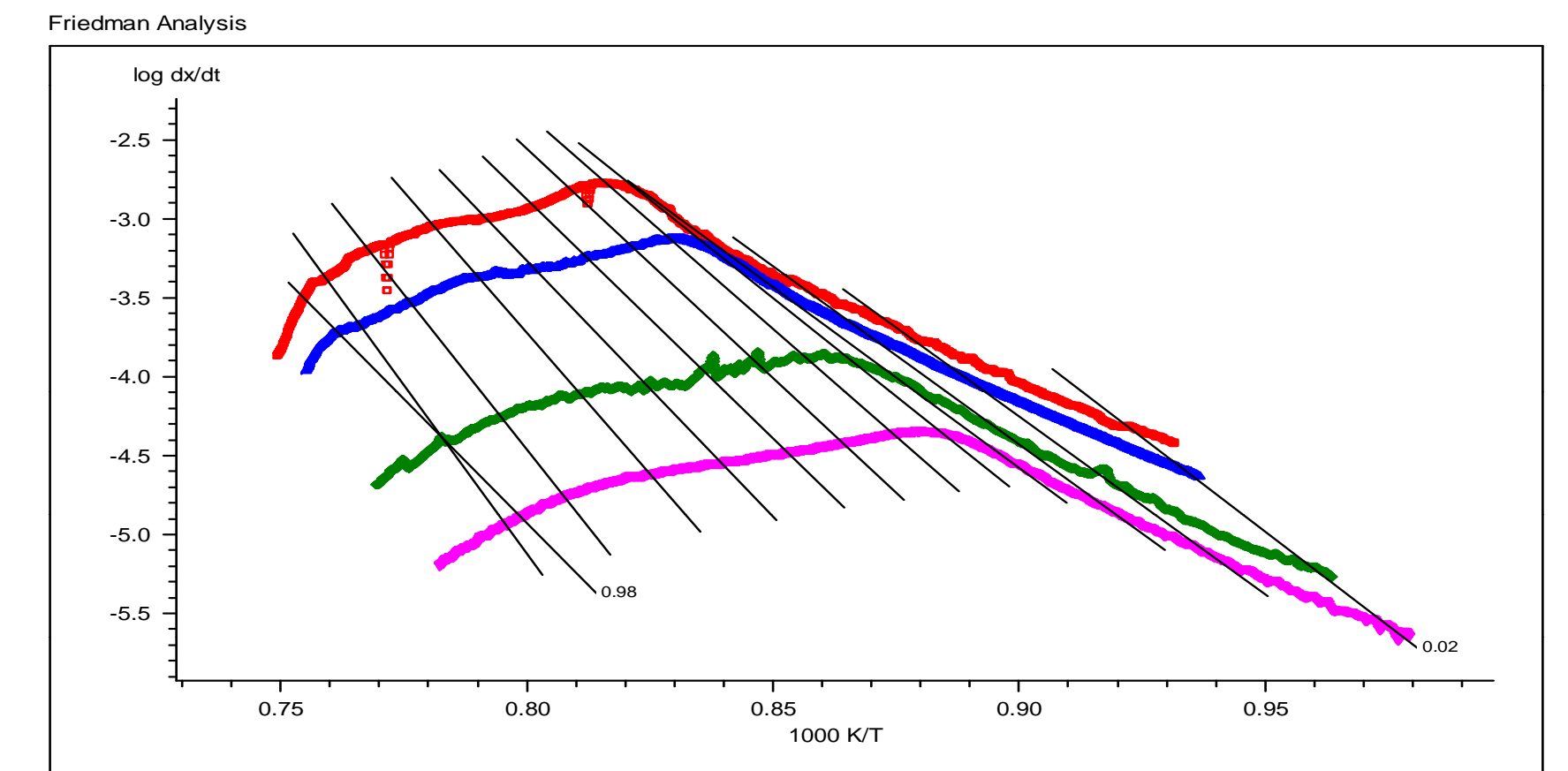
**Acknowledgements:** Help from C. Günter, P. Nielsen and A. Hoff is gratefully acknowledged.



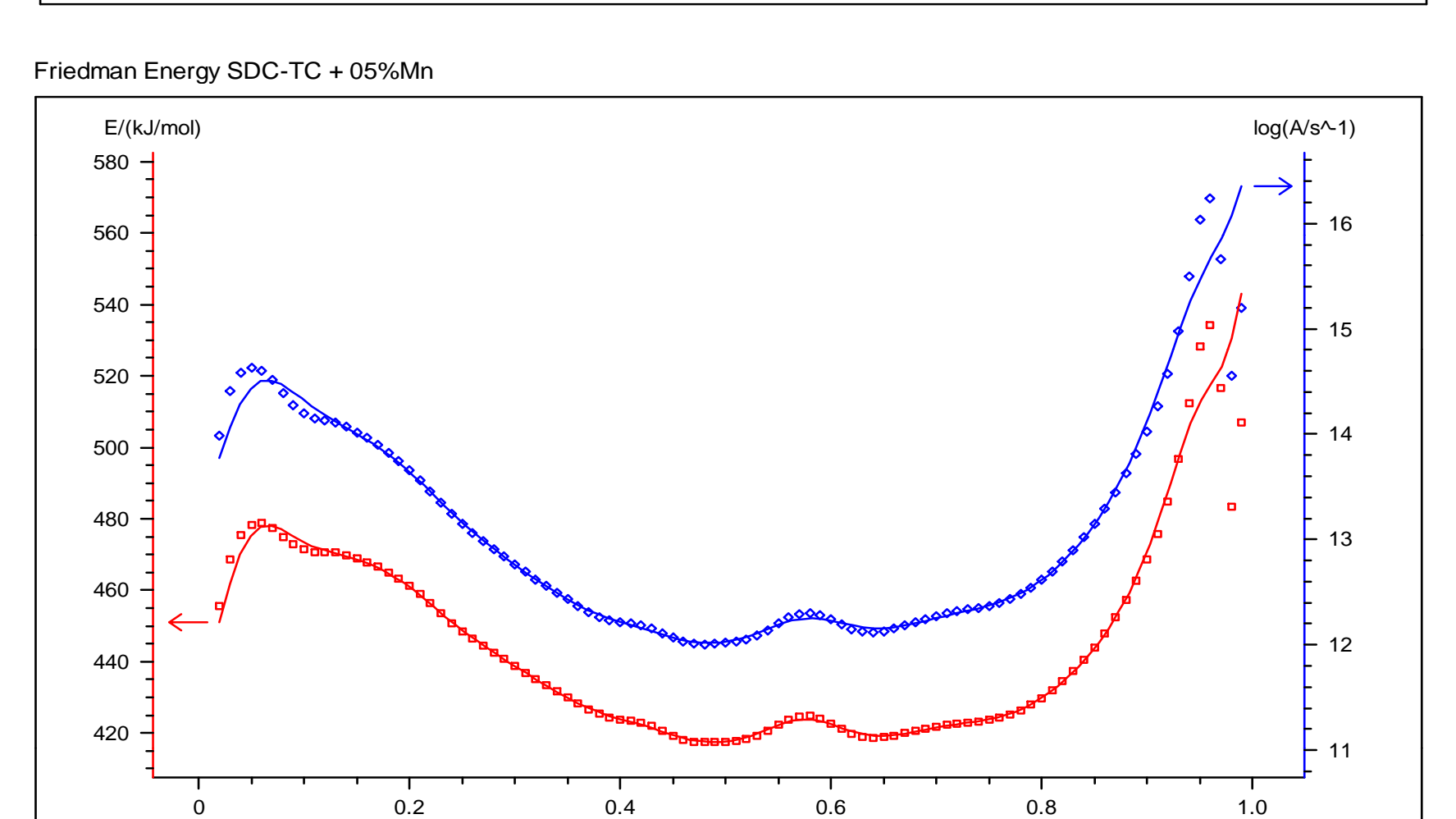
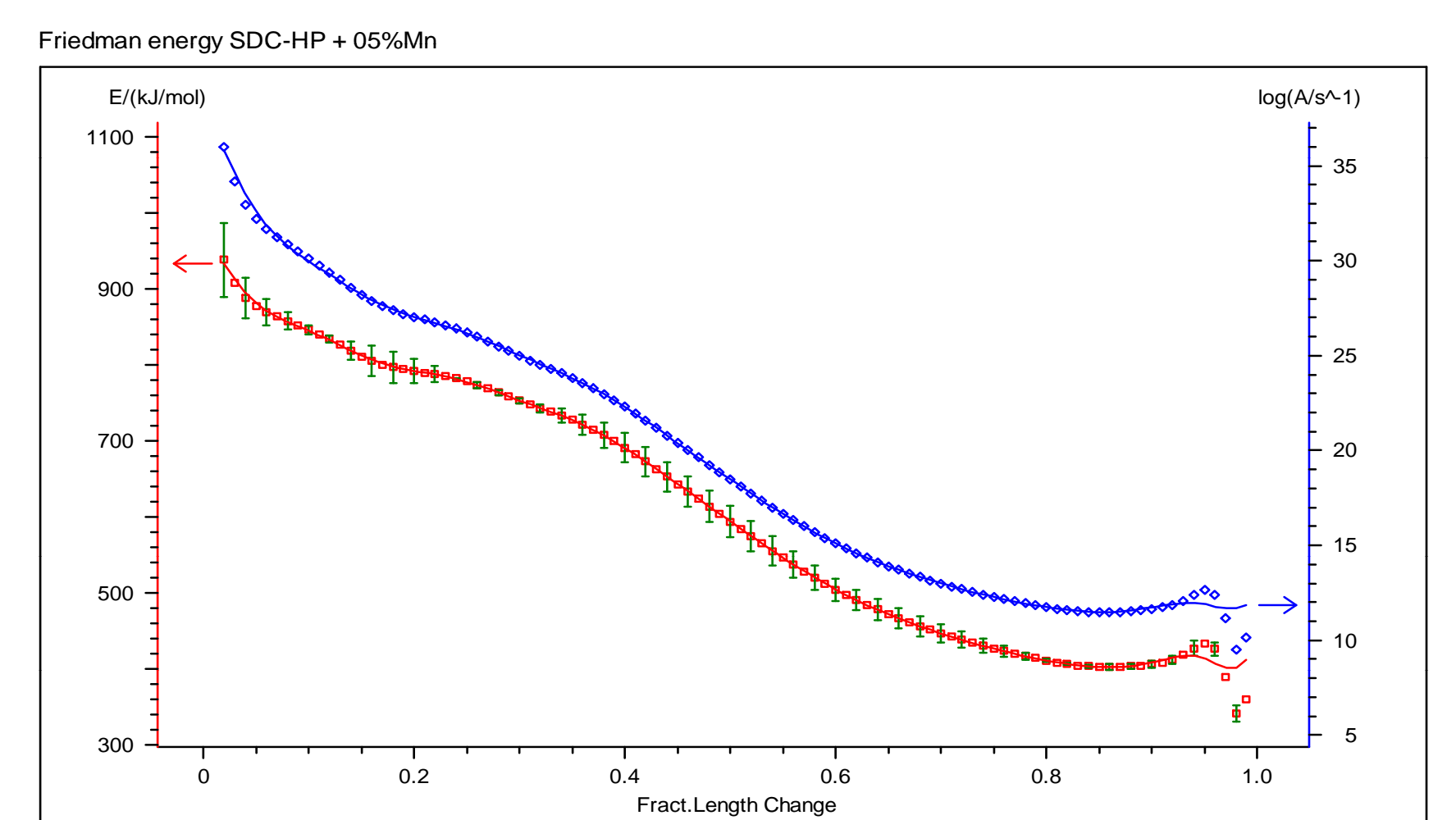
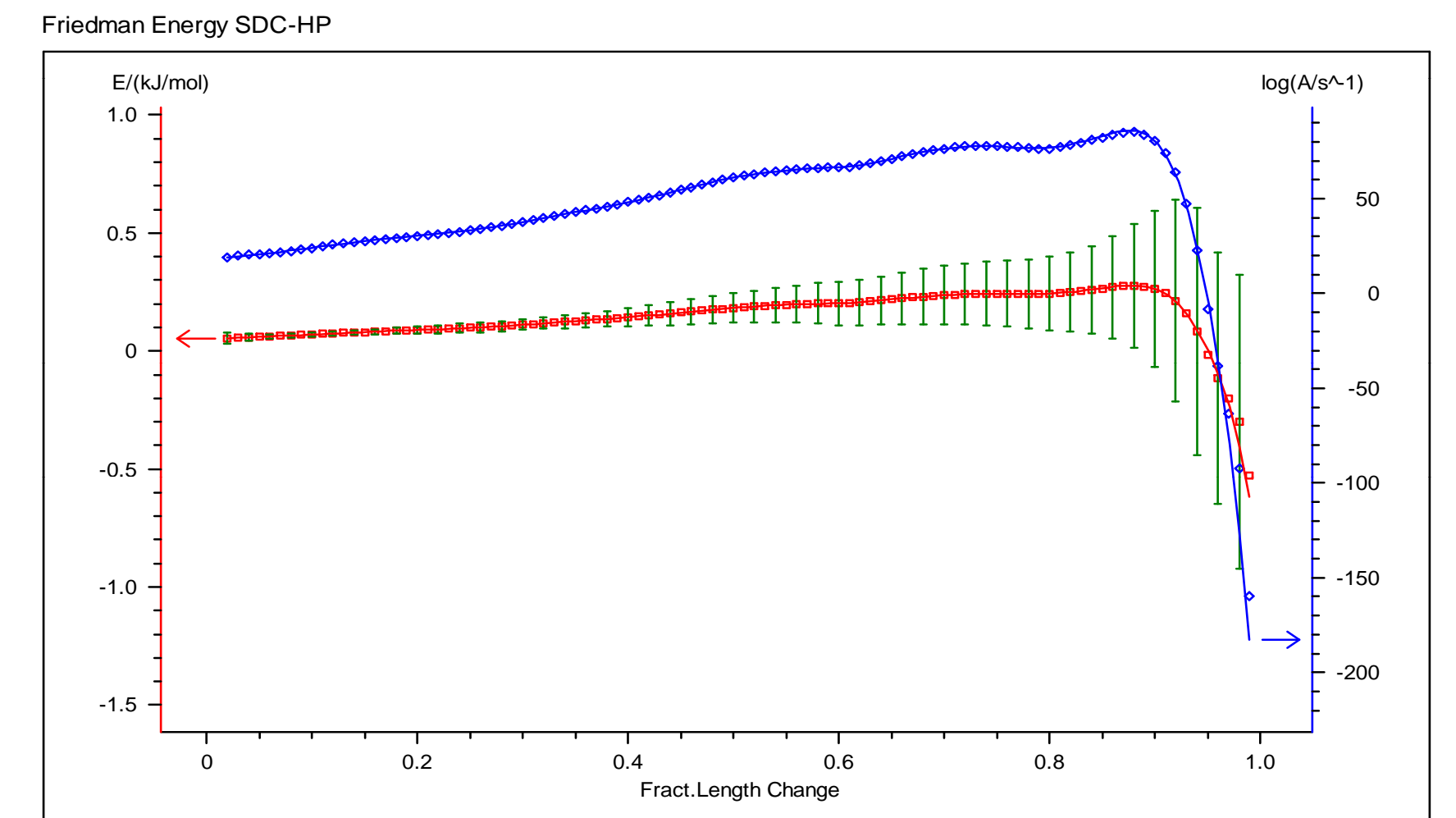
**Figure 1:** Relative sintering shrinkage and sintering rates for CGO10 and with sintering aids



**Figure 3:** Activation energy (red) and pre-exponential factor (blue) for CGO10 (upper) CGO10+2%Cu (middle) and CGO10+2%Mn (lower), Friedman (1965)



**Figure 2:** Conversion rate –  $\log(dx/dt)$  – versus inverse temperature for four heating rates of CGO10 with 2% Cu. Straight lines through iso-conversion points define activation energy, Friedman (1965)



**Figure 4:** Activation energy (red) and pre-exponential factor (blue) for SDC-HP (upper) SDC-HP+0.5%Mn (middle) and SDC-TC+0.5%Mn (lower)

## Conclusion and outlook

Analysis of the kinetic field was able to reveal qualitatively, differences in the sintering mechanisms and through further modeling work it is the aim to reach an even better understanding of the densification mechanisms, grain boundary chemistry and possibly also define optimum firing profiles for sintering the multi-layered cells

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